



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b> C07C 17/38, 17/10, 17/04 C07C 19/08	<b>A1</b>	<b>(11) International Publication Number:</b> WO 93/12058 <b>(43) International Publication Date:</b> 24 June 1993 (24.06.93)
<b>(21) International Application Number:</b> PCT/US92/10569 <b>(22) International Filing Date:</b> 9 December 1992 (09.12.92)  <b>(30) Priority data:</b> 809,808 18 December 1991 (18.12.91) US  <b>(71) Applicant:</b> ALLIED-SIGNAL INC. [US/US]; 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US).  <b>(72) Inventors:</b> YATES, Stephen, Frederic ; 5500 Carriageway Drive, #214C, Rolling Meadows, IL 60008 (US). HARNISH, Daniel, Franklin ; 77 Middlebury Road, Orchard Park, NY 14127 (US). SMITH, Addison, Miles ; 80 Berryman Drive, Amherst, NY 14226 (US).		<b>(74) Agent:</b> FUCHS, Gerhard, H.; Allied-Signal Inc., Law Department (C.A. McNally), 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US).  <b>(81) Designated States:</b> AU, BB, BG, BR, CA, CS, FI, HU, JP, KP, KR, LK, MG, MN, MW, NO, PL, RO, RU, SD, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, SN, TD, TG).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> PROCESS FOR REMOVING 2-CHLORO-1,1-DIFLUOROETHYLENE FROM 1,1,1,2-TETRAFLUOROETHANE AND CO-PRODUCING 2-CHLORO-1,1,1,2-TETRAFLUOROETHANE  <b>(57) Abstract</b>  2-Chloro-1,1-difluoroethylene (R-1122) is removed from 1,1,1,2-tetrafluoroethane (R-134a) by contacting the R-134a in the vapor phase with chlorine in the presence of ultraviolet light providing an exposure of at least about 2 watts-hour/kg.		

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PROCESS FOR REMOVING 2-CHLORO-1,1-DIFLUOROETHYLENE FROM  
1,1,1,2-TETRAFLUOROETHANE AND CO-PRODUCING  
2-CHLORO-1,1,1,2-TETRAFLUOROETHANE

5 BACKGROUND OF THE INVENTION

This invention relates principally to the purification of 1,1,1,2-tetrafluoroethane, also designated R-134a, which has been of particular interest as a replacement for chlorofluorocarbons having similar physical properties, particularly R-12. R-134a may be prepared by reaction of other fluorocarbons, such as trichloroethylene or R-133a (2-chloro-1,1,1-tri-  
10 fluoroethane) with HF. It may also be prepared by hydrogenation of R-114a (2,2-dichloro-1,1,1,2-tetrafluoroethane) or R-124 (2-chloro-1,1,1,2-tetrafluoroethane).  
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It is characteristic of such reactions that many by-products are formed, containing varying numbers of hydrogen, chlorine, and fluorine atoms on methane, ethane, and ethylene molecules. These by-products and the unreacted feed material may be separated by distillation where possible. Some compounds are relatively harmless since their presence does not greatly alter the physical properties for which HFC-134a is useful. A by-product which must be removed because of its toxicity is 2-chloro-1,1-difluoroethylene (R-1122), although only relatively small amounts are typically present in R-134a as formed. R-1122 has a boiling point close to that of R-134a making them difficult to separate  
20 by distillation. After distillation of the crude product, R-1122 will still be present in amounts from about 500 to 10,000 ppm (wt.). It should be reduced to below 10 ppm according to the specifications of the Panel for Advancement of Fluorocarbon Test (PAFTII).  
25 Preferably, the R-1122 should be below about 1 wt. ppm.  
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In U.S. Patent 3,819,493 Fozzard discloses an extractive distillation process for separating 1,1-difluoroethane (R-152a) from R-134a produced by  
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mixture with 1-4 mols of chlorine for each mol of R-1122 in the vapor phase in the presence of ultraviolet light having a wave length between about 300 to 400 nm which provides at least 2 watts-hour/kg of the mixture. The R-1122 can be reduced to below 35 wt. ppm or lower, as it is converted to 1,1,2-trichloro-1,1-difluoroethane (R-122), which has a higher boiling point and can be easily separated from R-134a. Other unsaturated compounds are also removed by chlorination to other derivatives which can be separated.

The photochlorination of R-134a may produce as a by-product 2-chloro-1,1,1,2-tetrafluoroethane (R-124). Since this is a useful product, the loss of R-134a is not necessarily a serious problem. In fact, co-production of R-124 may be desirable. Thus, in one aspect, the invention comprises a method for reducing the R-1122 in R-134a to a low level while producing R-124 along with R-134a. Alternatively, R-124 may be produced by photochlorination of R-134a in the absence of any need to remove R-1122. In another aspect, the invention includes a process for producing R-122 from R-1122.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph showing concentration at various ratios of chlorine to R-1122.

Figure 2 is a graph similar to Figure 1 including higher ratios of chlorine to R-1122.

#### DETAILED DESCRIPTION OF THE INVENTION

Typically HFC-134a is produced by reacting trichloroethylene or R-133a with HF over a catalyst and will contain a variety of byproducts such as R-143a, R-1122, R-124, R-133a, R-114a. It is of particular importance to remove 2-chloro-1,1-difluoroethylene (R-1122) from the crude product. Preliminary separation of R-134a by distillation will leave about 500 to 10,000 wt.

Cl<sub>2</sub>/R-1122 ratios are used. The Cl<sub>2</sub>/R-1122 ratio and UV exposure may be adjusted to provide the desired set of conditions. It is believed that the actual concentration of R-1122 is much lower than 35 wt. ppm. The presence of  
5 R-124a obscures the measurement of R-1122 at such low levels. Other analyses indicate that the combined amount of R-124a and R-1122 is mainly R-124a and, consequently, the actual amount of R-1122 is believed to be below 10 wt. ppm and thus should meet the desired specification.

10 The temperature employed may vary but may be from about -30°C to 200°C, preferably about 0° to 80°C.

The pressure selected will be a convenient value to suit the processing conditions for R-134a and to assure that R-134a is a vapor or liquid as desired.

15 The UV radiation from a lamp ordinarily will be expressed as watts, which is a rate of delivering energy. For present purposes, it is considered more useful to express radiation as the quantity of energy delivered over a period of time, i.e. the "exposure," rather than  
20 as the rate. Thus, the exposure may be expressed as watts-hours, which is related to the number of photons of energy delivered and their wavelength and these, in turn, relate to the chlorination of unsaturated molecules such as R-1122. Since the exposure is the product of the rate  
25 of delivering energy (photons/time) and the time, it will be clear that either the rate or the time could be varied. However, for practical applications the rate and the time will have limits imposed by the need to carry out the desired photochlorination reaction within  
30 constraints of time and product yield. If a high rate or a long time is used, not only will R-1122 be chlorinated to R-122, but chlorine will react with other molecules, particularly with R-134a to make HCFC-124. Alternatively, if a very low rate or a short time is  
35 used, then insufficient chlorination of R-1122 would be expected.

conditions this procedure gave an incident light intensity of  $1.448 \times 10^{-6}$  einstein/sec (0.497 watts). (One einstein is an equal to a mol of photons.)

Two feed streams were passed through separate  
5 lengths of capillary tubing and then mixed and passed into the reactor at 5 psig (34.5 kPa gauge). The impure R-134a contained 6000 wt. ppm R-1122 plus other impurities including R-134 which is converted to R-124a by photochlorination. One stream contained impure R-134a  
10 while the second contained chlorine. By blending the two streams the ratio of chlorine to R-1122 was varied. The radiation exposure was calculated from the residence time and the light intensity and varied from 5.89 to 27.5 watts-hour/kg. After exposure to the ultraviolet light  
15 the product stream was analyzed by gas chromatography using a 3048 mm long x 3.175 mm diameter column of 1% SP1000 on 60-80 mesh Carboxpack B (Supelco Inc.) packing operated at 45°C for 3 minutes and then programmed to increase 8°C/min to 200°C. As previously noted, R-124a  
20 and R-1122 are seen in this analysis as a single compound, consequently, the reported value for R-1122 is considered to be much below 35 wt. ppm and likely below 10 wt. ppm. It is to be understood that the figure 35 wt. ppm R-1122 represents the maximum value and in  
25 practice would be adjusted to account for R-124a.

The results of the tests at lower ratios of  $\text{Cl}_2/\text{R-1122}$  are given in Figure 1. The compounds are designated as refrigerants (R) according to the commonly used system of the American Society of Refrigerating  
30 Engineers.

It can be seen that the concentration of R-1122 decreases as the ratio of  $\text{Cl}_2/\text{R-1122}$  is increased. Theoretically one mol of chlorine can react with one mol of R-1122 to yield one mol of R-122. The results show  
35 that at a ratio of about 1.6/1 essentially all of the R-1122 has been converted within the limits of analytical

production of R-124 from R-134a and more generally, processes in which R-134a is converted to R-124 or R-1122 is converted to R-122.

an exposure greater than zero and up to about 1000 watts-hour/kg of said R-134a to produce R-124 by phot chlorination;

(b) separating the R-124 produced in (a) from  
5 R-134a.

7. The process of Claim 6 wherein R-124 is up to 16% based on the R-134a feed to the chlorination of step (a).

8. The process of Claim 6 wherein the mol ratio of  
10 chlorine to R-134a is greater than zero up to about 0.24/1.

9. A process for producing 1,2,2-trichloro-1,1 difluoroethane (R-122) from 2-chloro-1,1-difluoroethylene (R-1122) comprising

15 (a) contacting a mixture containing R-1122 with up to about 1-50 mols of chlorine for each mol of R-1122 in the presence of ultraviolet light having wavelengths between about 300 and 400 nm providing an exposure greater than zero and up to about 1000 watts-hour/kg of said R-1122, thereby producing R-122;  
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(b) separating the R-122 formed in (a) from R-1122.

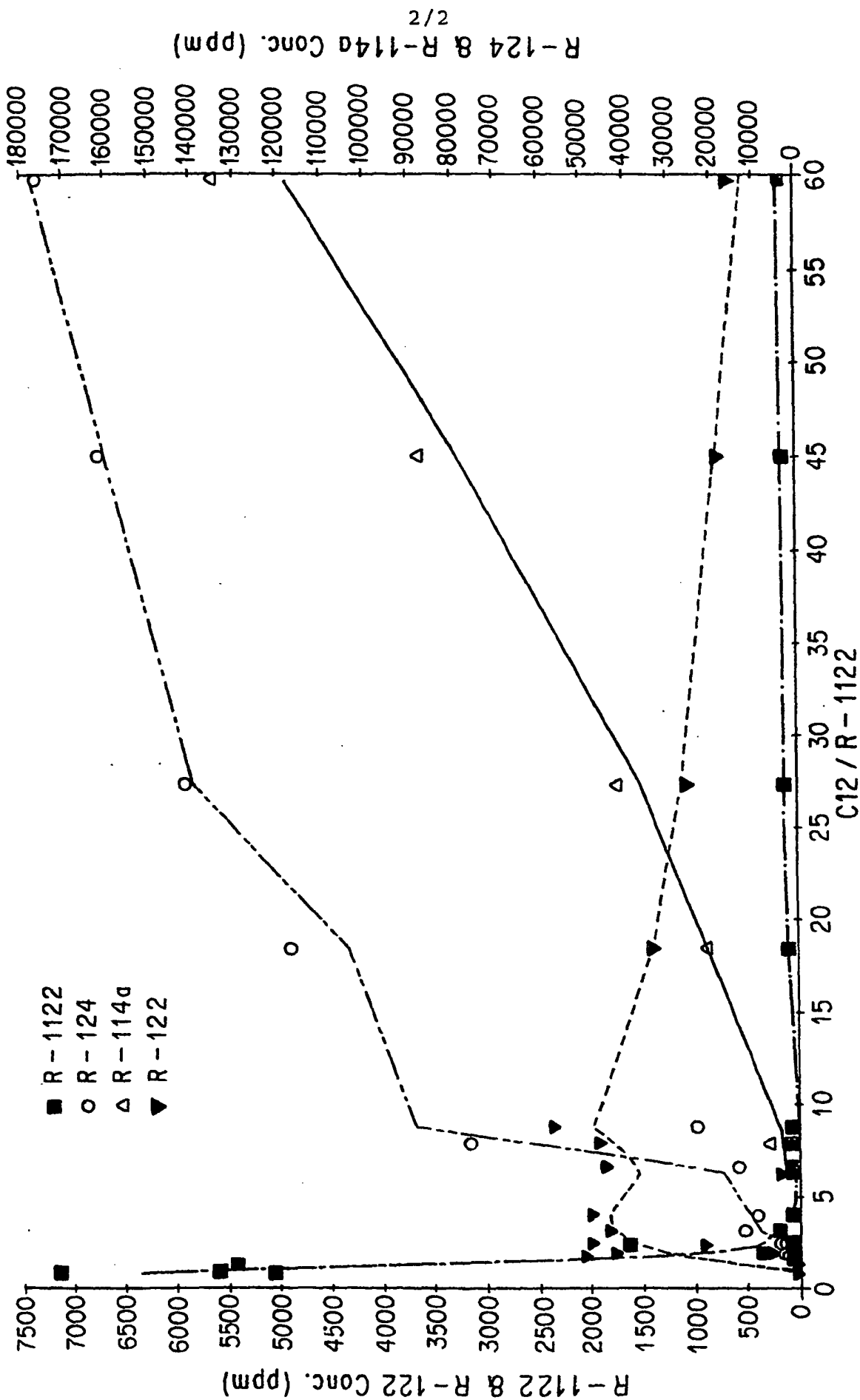


FIG. 2



## III. DOCUMENTS CONSIDERED TO BE RELEVANT

(CONTINUED FROM THE SECOND SHEET)

Category <sup>o</sup>	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	EP,A,0 346 612 (DAIKIN INDUSTRIES) 20 December 1989 see claims; examples -----	6-8